

POWER CABLE COMPOSITIONS FOR STRIPPABLE ADHESION

This invention relates to power cable compositions. Specifically, it relates to semiconductive power cable compositions, articles (such as a semiconductive cable layer and power cable constructions) prepared from the semiconductive compositions, and processes for preparing the semiconductive compositions and related articles.

5 Power cables, rated for a conductor operating temperature of 90-degree Centigrade or higher, are commonly prepared by extruding chemically-crosslinkable polymer materials around the conductor. Following extrusion, the chemically-crosslinkable polymeric materials are crosslinked to resist material deformation at the rated cable operating temperature and related overload conditions.

10 For medium- and high-voltage cable designs, the chemically-crosslinkable polymeric materials commonly contain conductive fillers to render the resulting cable layer semiconductive. The chemically-crosslinkable polymeric materials are extruded to prepare an electrical stress control layer between the metallic conductor and a polymer-dielectric insulation layer and may also be used as an electrical stress control
15 layer between the polymer dielectric layer and grounding wires or tapes. The various layers are typically co-extruded and subsequently, simultaneously crosslinked. In addition, some cable constructions can include protective sheaths, moisture barriers, or protective jackets.

20 Co-extrusion and simultaneous crosslinking are generally desirable because the resulting cable layers are closely bonded. Close bonding prevents partial delamination of the layers and precludes void forming between the layers, thereby preventing premature cable failure. Delamination and void formation can result from flexure and/or heat during the normal use of the cable.

Unfortunately, close bonding as a result of co-extrusion and simultaneous crosslinking is not free of disadvantages. Notably, the method of manufacture presents problems for applications in which stripping the outermost electrical stress control layer (or semiconductive layer) from the polymer-dielectric insulation layer is desirable. (It is believed that crosslinking bond occur across the interface between the electrical stress control layer and the polymer-dielectric insulation layer. Those bonds must be broken to strip the layers apart.) Stripping the semiconductive layer away from the insulation layer damages the insulation layer when the force to separate the layers is excessive.

It is desirable for the semiconductive layer to adhere to the insulation layer under normal operating conditions while being easily strippable from the insulation layer on demand. These features promote utilization of the cable for its normal life and ease of installation of such accessories as joints, splices, and terminations.

Currently, the chemically-crosslinkable polymeric materials often contain polar polymers to reduce their melt miscibility with insulation materials, which generally contain non-polar polyolefinic polymers. Most commonly, the chemically-crosslinkable polymer materials are based upon ethylene vinyl acetate copolymers, having a vinyl acetate comonomer content of greater than 28% by weight. A disadvantage of these high-polarity copolymers is that they tend to yield compounds prone to agglomeration. It is desirable to avoid the problem of agglomeration.

The present invention is a semiconductive power cable composition comprising (a) a mixture of a high-temperature polymer and a soft polymer, and (b) a conductive filler, wherein a semiconductive cable layer prepared from the composition strippably adheres to a second cable layer. The invention also includes a semiconductive cable layer prepared from the semiconductive power cable

composition as well as a power cable construction prepared by applying the semiconductive cable layer over a wire or cable.

Moreover, the present invention includes a process for preparing the semiconductive power cable composition comprising the step of blending a mixture
5 of a high-temperature polymer, a soft polymer, and a conductive filler. Alternatively, the process comprises the steps of (a) reactively-coupling a mixture of a high-temperature polymer, a soft polymer, and a first coupling agent, in the presence of a conductive filler and wherein the resulting mixture having a reduced curative level, and (b) admixing a second coupling agent, wherein the second coupling agent does
10 not substantially affect the curative level of the resulting mixture.

The present invention also includes a process for preparing a power cable comprising the steps of (a) extruding a power cable semiconductive composition over a metallic conductor to yield a semiconductive cable layer over the metallic conductor, (b) extruding a chemically-crosslinkable insulation composition over the
15 semiconductive cable layer, (c) extruding a second semiconductive power cable composition over the polymer-dielectric insulation to yield a second semiconductive cable layer, and (d) crosslinking the chemically-crosslinkable insulation composition to yield a crosslinked, polymer-dielectric insulation.

The invented semiconductive power cable composition comprises (a) a
20 mixture of a high-temperature polymer and a soft polymer and (b) a conductive filler, wherein a semiconductive cable layer prepared from the composition strippably adheres to a second cable layer. Preferably, the resulting semiconductive cable layer with have a heat resistance of less than 100% as measured by a Hot Creep test at a testing temperature of 150 degrees Centigrade (Test Method described in ICEA T-28-
25 562, and referenced in ANSI/ICEA Standards S-94-649 and S-97-682).

As the term is used herein, "strippably adheres" means that the semiconductive layer adheres to a second layer (usually, an insulation layer) under normal operating conditions of the power cable while having the property of being easily strippable from the second layer (i.e., delaminating/separating the semiconductive layer from the second layer without substantially damaging the second layer) on demand. With reference to strip tension, the term "strippably adheres" means a strip tension between 3 and 24 pounds per 0.5 inch wide strip (1.3 to 10.9 kilograms per 13 millimeter wide strip). This test method is also is also referenced in ANSI/ICEA Standards S-94-649 and S-97-682.

A high-temperature polymer, as that term is used herein, means a polymer having suitable heat resistance for the semiconductive cable layer but lacking other desirable properties. For example, the high-temperature polymer may not have desirable processing characteristics or other material properties. Suitable high-temperature polymers include polypropylenes, polyesters, nylons, polysulfones, and polyaramides. Preferred high-temperature polymers are polypropylenes. The high temperature polymer is preferably in the composition in an amount less than 50 weight percent. More preferably, the high temperature polymer is present in an amount between 10 and 40 weight percent. Most preferably, it is present in an amount between 20 and 30 weight percent.

A soft polymer, as that term is used herein, means a polymer that enhances the processing characteristics of the high-temperature polymer and provides a networking source as the soft polymer is coupled to the high-temperature polymer for additional heat resistance. Suitable soft polymers include polyethylenes, polypropylenes, polyesters, and rubbers. Preferred soft polymers are polyethylenes.

Polyethylenes include homopolymers of ethylene and copolymers of ethylene and one or more alpha-olefins, and, optionally, a diene. The polyethylene can also be a copolymer of ethylene and an unsaturated ester such as a vinyl ester (e.g., vinyl acetate or an acrylic or methacrylic acid ester), a copolymer of ethylene and an unsaturated acid such as acrylic or methacrylic acid, or a copolymer of ethylene and a vinyl silane (e.g., vinyltrimethoxysilane and vinyltriethoxysilane) as well as interpolymers of any of these comonomers. Post-modified polyethylenes of any other of the above are considered within the scope of this invention as well as blends thereof. Preferred polyethylenes are homopolymers of ethylene, copolymers of ethylene and one or more alpha-olefins, and a copolymer of ethylene and an unsaturated ester. More preferred polyethylenes for soft polymers are copolymers of a polar monomer and a nonpolar comonomer. Most preferred polyethylenes are copolymers of ethylene and an unsaturated ester.

Suitable polypropylenes include homopolymers of propylene, copolymers of propylene and other olefins, and terpolymers of propylene, ethylene, and dienes.

Suitable polyesters include thermoplastic resins comprising a saturated dicarboxylic acid and a saturated difunctional alcohol. Specific examples include polyethylene terephthalate, polypropylene terephthalate (or trimethylene terephthalate), polybutylene terephthalate, polytetramethylene terephthalate, polyhexamethylene terephthalate, polycyclohexane-1,4-dimethylol terephthalate, and polyneopentyl terephthalate. Preferred polyesters are polyethylene terephthalate, polypropylene terephthalate (or trimethylene terephthalate), and polybutylene terephthalate.

Suitable nylons include nylon 6, nylon 6,6, and nylons based upon longer chain-length diamines. Preferred nylons are nylon 6 and nylon 6,6.

Suitable rubbers include thermoplastic rubbers, ethylene propylene diene rubber, styrene-butadiene block copolymers, styrene-butadiene rubber, polybutadiene rubbers, isoprene rubbers, nitrile rubbers, polychloroprene rubbers, hydrogenated styrene-butadiene block copolymers, methacrylate butadiene styrene rubber, acrylic
5 elastomers (such ethylene methylacrylate), fluoroelastomers, and thermoplastic elastomers (such as thermoplastic urethanes, polyamids, and polyester ethers).

Suitable conductive fillers include carbon blacks, carbon fibers, carbon nanotubes, graphite particles, metals, and metal-coated particles. Preferred
10 conductive fillers are carbon blacks. Preferably, the conductive filler will be present in the composition in an amount sufficient to impart a volume resistivity of less than 50,000 ohm-cm for a semiconductive cable layer prepared therefrom, as measured by the methods described in ICEA S-66-524.

In addition, a curing agent may be present in the semiconductive composition. Suitable curing agents include organic peroxides, azides, organofunctional silanes,
15 maleated polyolefins, phenols, and sulfur vulcanizing agents. Suitable organic peroxides include aromatic diacyl peroxides, aliphatic diacyl peroxides, dibasic acid peroxides, ketone peroxides, alkyl peroxyesters, and alkyl hydroperoxides. Suitable azide curing agents include alkyl azide, aryl azides, acyl azides, azidoformates, phosphoryl azides, phosphinic azides, silyl azides, and polyfunctional azides.
20 Suitable silanes include unsaturated silanes that comprise an ethylenically unsaturated hydrocarbyl group, such as a vinyl, allyl, isopropenyl, butenyl, cyclohexenyl or γ -(meth)acryloxy allyl group, and a hydrolyzable group, such as, for example, a hydrocarbyloxy, hydrocarbonyloxy, or hydrocarbylamino group. Preferred curing agents are organic peroxides.

In addition, the semiconductive power cable composition may further comprise a coupling agent. The term "coupling agent," as used herein, means a compound or mixture of compounds used for the purposes of coupling or grafting a polymer or polymer blend. The coupling agent may be present in an amount
5 sufficient to reduce the amount of a curing agent required to impart heat resistance to the semiconductive cable layer. The coupling agent may be the same compound as the curing agent..

Suitable coupling agents include organic peroxides, azides, organofunctional silanes, maleated polyolefins, phenols, and sulfur vulcanizing agents. Suitable
10 organic peroxides include aromatic diacyl peroxides, aliphatic diacyl peroxides, dibasic acid peroxides, ketone peroxides, alkyl peroxyesters, and alkyl hydroperoxides. Suitable azide coupling agents include alkyl azide, aryl azides, acyl azides, azidoformates, phosphoryl azides, phosphinic azides, silyl azides, and polyfunctional azides. Suitable silanes include unsaturated silanes that comprise an
15 ethylenically unsaturated hydrocarbyl group, such as a vinyl, allyl, isopropenyl, butenyl, cyclohexenyl or γ -(meth)acryloxy allyl group, and a hydrolyzable group, such as, for example, a hydrocarbyloxy, hydrocarbonyloxy, or hydrocarbylamino group. Preferred coupling agents are organic peroxides.

In addition, the semiconductive power cable composition may further
20 comprise a compatibilizing polymer. As used herein, the term "compatibilizing polymers" includes those polymers having an affinity for both the high-temperature polymer and the soft polymer. Preferred compatibilizing polymer are copolymers (such as ethylene-alpha-olefin copolymers) and functionalized polymers (such as maleated polyolefins and glycidil-functional polyolefins). Based on the selection of

the high-temperature and soft polymers, a person skilled in the art can readily identify other suitable compatibilizing polymers.

In addition, the composition may contain other additives such as antioxidants, stabilizers, blowing agents, pigments, processing aids, and cure boosters.

5 In a preferred embodiment, the present invention is a semiconductive power cable composition comprising (a) a mixture of a high-temperature polymer and a soft polymer and (b) a conductive filler, wherein a semiconductive cable layer prepared from the composition strippably adheres to a second cable layer. The high-temperature polymer and the soft polymer may have different heat resistance. In a
10 more preferred embodiment, the semiconductive cable layer has a heat resistance of less than 100% as measured by a Hot Creep test at a testing temperature of 150 degrees Centigrade. Also, in a more preferred embodiment, the second cable layer is a chemically-crosslinked layer.

In an alternate embodiment, a semiconductive cable layer is prepared from the
15 semiconductive power cable composition. In a yet another embodiment, a power cable construction is prepared by applying the semiconductive cable layer over a wire or cable.

In another alternate embodiment, the present invention is a process for preparing a semiconductive power cable composition comprising the step of blending
20 a mixture of a high-temperature polymer, a soft polymer, and a conductive filler, wherein a semiconductive cable layer prepared from the composition strippably adheres to a second cable layer. In this embodiment, the mixture may further comprise a coupling agent. Preferably, the coupling agent reduces the amount of a curing agent required to impart heat resistance to a semiconductive cable layer

prepared from a mixture of the high-temperature polymer, the soft polymer, and the conductive filler in the absence of the coupling agent.

In yet another embodiment, the invention is a process for preparing a semiconductive power cable composition comprising the steps of (a) reactively-
5 coupling a mixture of a high-temperature polymer, a soft polymer, and a coupling agent, in the presence of a conductive filler, and (b) admixing a curing agent, wherein a semiconductive cable layer prepared from the composition strippably adheres to a second cable layer. Preferably, the coupling agent reduces the amount of the curing agent required to impart heat resistance to a semiconductive cable layer prepared from
10 a mixture of the high-temperature polymer, the soft polymer, and the conductive filler in the absence of the coupling agent.

In another embodiment of the present invention, the invention is a process for preparing a power cable comprising the steps of (a) extruding a semiconductive power cable composition comprising a mixture of a high-temperature polymer, a soft
15 polymer, and a conductive filler, over a metallic conductor to yield a semiconductive cable layer over the metallic conductor, and (b) extruding a polymer-dielectric insulation over the semiconductive cable layer. This embodiment may further comprise the step of (c) extruding a second semiconductive power cable composition over the polymer-dielectric insulation to yield a second semiconductive cable layer.

20 In an alternate aspect of this embodiment, the invention is a process comprising the steps of (a) extruding a power cable semiconductive composition comprising a mixture of a high-temperature polymer, a soft polymer, and a conductive filler, over a metallic conductor to yield a semiconductive cable layer over the metallic conductor, (b) extruding a chemically-crosslinkable insulation composition
25 over the semiconductive cable layer, (c) extruding a second semiconductive power

cable composition over the polymer-dielectric insulation to yield a second semiconductive cable layer, and (d) crosslinking the chemically-crosslinkable insulation composition to yield a crosslinked, polymer-dielectric insulation.

EXAMPLES

5 The following non-limiting examples illustrate the invention.

Examples 1-7

In Comparative Examples 1, 6, and 7 and Examples 2, 4, and 5, the mixtures were combined in a lab-scale compounder to achieve a melt temperature of 190 degrees Centigrade for 5 minutes. In Example 3, the mixture of the high-temperature
10 polymer, the soft polymer, and the conductive filler were combined in a lab-scale compounder to achieve a melt temperature of 190 degrees Centigrade for 5 minutes and then allowed to cool; then the peroxide was added at 120 degrees Centigrade.

Each exemplified formulation was evaluated for Hot Creep performance and adhesion to a polyethylene-insulation substrate. The Hot Creep test specimens were
15 evaluated for their resistance to thermal deformation under load conditions of 20 N/sq. cm. tensile stress for 15 minutes at 150 degrees Centigrade. Elongation and residual deformation were measured. Residual deformation is reported in Table I as % Hot Set.

For the adhesion measurement, 30 mil plaques of the exemplified formulations
20 were prepared. A polyethylene-insulation substrate was prepared from The Dow Chemical Company's commercially available HFDB-4202 crosslinkable polyethylene insulation at 120 degrees Centigrade. Subsequently, the test plaques and the polyethylene-insulation substrate were molded together under pressure at a temperature in excess of 180 degrees Centigrade for a length time sufficient for the
25 substrate to cure. Next, the dual-layer specimens were conditioned at ambient

temperature overnight. A one-half inch wide strip was scored from the dual-layer specimen. A 90-degree peel test was performed in an INSTRON™ tensile machine at a peel rate of 20 inches per minute.

The polymeric materials for the exemplified formulations were added in the concentrations shown in Table I and include:

- (1) duPont Elvax 265™ ethylene vinylacetate copolymer (EVA-1), having a vinylacetate content of 28% by weight and a melt index of 3 g/10minutes;
- (2) DXM-451™ ethylene vinylacetate copolymer (EVA-2), having a vinylacetate content of 18% by weight and a melt index of 3 g/10minutes and commercially available from The Dow Chemical Company;
- (3) 5D45™ polypropylene (PP-1), which was a fractional homopolymer having a melt flow rate of 0.8 and commercially available from The Dow Chemical Company; and
- (4) a homopolymer of polypropylene (PP-2) having a melt flow rate of 20.

The carbon black was CSX614 and commercially available from Cabot Corporation. Each formulation contained 55 parts per hundred polymer (pphr) of carbon black. The peroxide used was TRIGANOX 101, and commercially available from Akzo Nobel. For Comparative Example 1 and Examples 2-5, the peroxide was added in the amount of 0.4 pphr during the compounding. For Comparative Example 6, the peroxide was added in the amount of 0.4 pphr following the compounding. The formulation for Comparative Example 7 did not contain any peroxide.

While the peroxide in the formulation exemplified as Comparative Example 1 was fully reacted during compounding, the test specimens were unable to withstand

the Hot Creep load. Without any residual unreacted peroxide, the test specimen for Comparative Example 1 was fully bonded to the polyethylene-insulation substrate. This bonding also demonstrates that, if the formulation had not contained any peroxide during the compounding, the resulting test specimen would have fully bond
5 itself to the polyethylene-insulation substrate and that current practices using EVA-2 would result in a fully-bonded test specimen.

Table I shows that formulation exemplified as Example 2 had desirable Hot Creep and strippability from the polyethylene-insulation substrate. While the Example 3 formulation showed improved heat resistance, its test specimens became
10 fully bonded to the polyethylene-insulation substrate. Examples 4 and 5 demonstrated formulations with improvements over the Example 2 formulation in heat resistance and strippability.

While Comparative Example 6 demonstrated excellent heat resistance, its unreacted peroxide (i.e., peroxide not consumed during compounding) did not
15 sufficiently reduce the curative level of the mixture to prevent the test specimens from fully bonding to the polyethylene-insulation substrate. Comparative Example 7, which is a blend with no coupling agent, yielded test specimens with relatively poor heat resistance.

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TABLE I

Component	Comp. Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp. Ex. 6	Comp. Ex. 7
EVA-1				65	65		
EVA-2	100	65	65			65	65
PP-1		35		35		35	35
PP-2			35		35		
Test							
Adhesion	Bonded	2.5 (strippable)	Bonded	1.1 (strippable)	3.8 (strippable)	Bonded	Bonded
Hot Creep %	Failed	27	18	18	18	0	56
Hot Set %	---	6.3	5.5	1.6	0.8	0.1	22

Example 8

In Example 8, a mixture was combined in a lab-scale compounder to achieve a melt temperature of 190 degrees Centigrade for 5 minutes. The mixture contained 65 parts of EVA-1, 35 parts of PP-1, 55 parts per hundred polymer (pphr) of Cabot Corporation CSX614 carbon black, and 0.4 pphr Akzo Nobel TRIGANOX 101 peroxide.

As part of a 15-kilovolt power cable design, the mixture was extruded as a semiconductive layer over a peroxide crosslinkable polyethylene insulation (HFDB-4202). The HFDB-4202 crosslinkable polyethylene insulation is available commercially from The Dow Chemical Company.

The 15-kilovolt power cable design used a 1/0 AWG aluminum conductor, 15 mils of a crosslinkable semiconductive power cable compound, 175 mils of the crosslinkable polyethylene insulation, and 40 mils of the semiconductive power cable composition of Example 8. The extruded cable was passed through a hot, dry nitrogen tube (continuous vulcanization tube) wherein the thermal decomposition of organic peroxide initiates polymer crosslinking. The cured cable was then passed through a cooling water trough.

The outer semiconductive power cable composition of Example 8 was found to strippably adhere to the crosslinked polyethylene cable insulation, having a strip tension of 11-12 pounds per 0.5 inches. It also had a Hot Creep elongation of 19% when tested at 150 degrees Centigrade and 0.2 MPa of applied tensile stress.